ELONGATED NANO-STRUCTURES AND RELATED DEVICES

STATEMENT REGARDING GOVERNMENT RIGHTS

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BACKGROUND

Field of the Invention

[0001] The invention relates to nano-scale structures and, more specifically, to elongated nano-structures.

Description of the Prior Art

[0002] Field emission devices (gated or ungated) have applications in X-ray imaging, medical imaging systems, displays, electronics, microwave amplifiers, fluorescent lamp cathodes, gas discharge tubes, and many other electrical systems. Other applications for field emission devices include sensors, photonic bandgap devices, and wide bandgap semiconductor devices.

[0003] Carbon nanotubes are currently being researched as electron emission sources in, for example, flat panel field emission display ("FED") applications, microwave power amplifier applications, transistor applications and electron-beam lithography applications. The carbon nanotubes are typically synthesized through an arc discharge method, a chemical vapor deposition (CVD) method or a laser ablation method. Carbon nanotubes offer the advantage of having high aspect ratios which increases the field enhancement factor and therefore the extraction of electrons at relatively low electric fields. Carbon nanotubes, however, exhibit a fairly high work function, and are prone to damage under typical operating conditions, limiting the life and effectiveness of the devices. What is needed therefore is a material more robust

and with a lower work function than carbon, but with a cylindrical geometry and diameters in the 10-100 nm range.

[0004] Carbide materials may be preferred due to their chemical stability, mechanical hardness and strength, high electrical conductivity, and relatively low work function. These characteristics make them particularly suited to the environment that may be found in a CT system. Such materials may also be important in superconducting nanodevices, opoelectronic nanodevices, and other similar systems.

[0005] Currently, the predominating approach to synthesizing carbide nanorods has been to use a carbon nanotube (CNT) as a template on which a reaction is carried out between the CNT and a metal, metal oxide, or metal iodide in vapor form to produce metal carbide nanarods. However, demonstration of CNT conversion in a device structure has not been shown to date, presumably owing to a number of risks associated with such a process, including the large volume changes (about 60% for CNTs that are converted to Mo_2C), adhesion to the substrate after conversion, and the ability to maintain alignment.

[0006] Therefore, there is a need for a system that does not require carbon nanotubes as template for carbide nanorod conversion

[0007] There is also a need for a system that grows elongated carbide nanostructures in situ directly in a gated structure.

[0008] There is also a need for a fabrication procedure that allows for seamless integration with gated device structures as well as control of the lateral density of the nanorods so that electric field shielding does not occur.

SUMMARY OF THE INVENTION

[0009] The disadvantages of the prior art are overcome by the present invention, which, in one aspect, is a method of making an elongated carbide nanostructure. A plurality of spatially-separated catalyst particles is applied to a substrate. The spatially-separated catalyst particles and at least a portion of the substrate are exposed to a metal-containing vapor at a preselected temperature and for a period sufficient to cause an inorganic nano-structure to form between the substrate and at least one of the catalyst particles. The inorganic nano-structure is exposed to a carbon-containing vapor source at a preselected temperature and for a period sufficient to carburize the inorganic nano-structure.

[0010] In another aspect, the invention is a method of making a field emission device. A dielectric layer is applied to a substrate. A conductive layer is applied to the dielectric layer, opposite the substrate. At least one cavity is formed in the conductive layer and the dielectric layer, thereby exposing the substrate. At least one nanorod is grown in the cavity.

[0011] In another aspect, the invention is a field emission device that includes a substrate that has a top side and an opposite bottom side. A dielectric layer is disposed on the top side. A conductive layer is disposed on top of the dielectric layer opposite the substrate. The conductive layer and the dielectric layer define a cavity extending downwardly to the substrate. At least one nanorod is affixed to the substrate and is substantially disposed within the cavity.

[0012] In another aspect, the invention is a nanostructure that includes an inorganic substrate having a top side and a bottom side. A conductive buffer layer is disposed adjacent to the top side. A plurality of elongated carburized metal nanostructures extend from the conductive buffer layer.

[0013] In another aspect, the invention is a field emission device that includes a substrate. The substrate has a top side and an opposite bottom side. A dielectric layer is disposed on the top side. A conductive layer is disposed on top of the dielectric layer opposite the substrate. The conductive layer and the dielectric layer define a cavity extending downwardly to the substrate. A conductive platform, having a top surface, is disposed on the top side of the substrate within the cavity. At least one nanorod extends upwardly from the top surface of the conductive platform and is substantially disposed within the cavity.

[0014] In yet another aspect, the invention is a structure that includes a polycrystalline nanorod. The polycrystalline nanorod is made of a material selected from: molybdenum carbide, molybdenum silicide, molybdenum oxycarbide, and niobium carbide.

[0015] These and other aspects of the invention will become apparent from the following description of the preferred embodiments taken in conjunction with the following drawings. As would be obvious to one skilled in the art, many variations and modifications of the invention may be effected without departing from the spirit and scope of the novel concepts of the disclosure.

BRIEF DESCRIPTION OF THE FIGURES OF THE DRAWINGS

[0016] FIG. 1A is a side elevational view showing a structure-growing step employed in one embodiment of the invention.

[0017] FIG. 1B is a side elevational view showing a carburizing step subsequent to the step shown in FIG. 1A.

[0018] FIG. 1C is a side elevational view showing an etching step subsequent to the step shown in FIG. 1B.

[0019] FIG. 1D is a side elevational view showing a carburized nano-structure formed subsequent to the step shown in FIG. 1C.

[0020] FIG. 2A is a side elevational view showing a structure-growing step employed in a second embodiment of the invention.

[0021] FIG. 2B is a side elevational view showing a carburizing step subsequent to the step shown in FIG. 2A.

[0022] FIG. 2C is a side elevational view showing an etching step subsequent to the step shown in FIG. 2B.

[0023] FIG. 2D is a side elevational view showing a carburized nano-structure subsequent to the step shown in FIG. 2C.

[0024] FIG. 3A a side elevational view showing a step in making a field emitter.

[0025] FIG. 3B is a side elevational view showing a step in making a field emitter according to one embodiment of the invention subsequent to the step shown in FIG. 3A.

[0026] FIG. 3C is a side elevational view showing a step in making a field emitter according to one embodiment of the invention subsequent to the step shown in FIG. 3B.

[0027] FIG. 3D is a side elevational view showing a step in making a field emitter according to one embodiment of the invention subsequent to the step shown in FIG. 3C.

[0028] FIG. 3E is a side elevational view showing a step in making a field emitter according to one embodiment of the invention subsequent to the step shown in FIG. 3D.

[0029] FIG. 4A is a side elevational view showing an alternate embodiment of making a field emitter.

[0030] FIG. 4B is a side elevational view showing a step subsequent to the step shown in FIG. 4A.

[0031] FIG. 4C is a side elevational view showing a step subsequent to the step shown in FIG. 4B.

[0032] FIG. 4D is a side elevational view showing a step subsequent to the step shown in FIG. 4C.

[0033] FIG. 4E is a side elevational view showing a step subsequent to the step shown in FIG. 4D.

[0034] FIG. 5A is a micrograph of a nanorod according to one embodiment of the invention.

[0035] FIG. 5B is a micrograph of a nanoribbon according to one embodiment of the invention.

[0036] FIG. 5C is a micrograph of a polycrystalline nanorod according to one embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0037] A preferred embodiment of the invention is now described in detail. Referring to the drawings, like numbers indicate like parts throughout the views. As used in the description herein and throughout the claims, the following terms take the meanings explicitly associated herein, unless the context clearly dictates otherwise: the meaning of "a," "an," and "the" includes plural reference, the meaning of "in" includes "in" and "on." Unless otherwise specified herein, the drawings are not necessarily drawn to scale.

[0038] Also, as used herein, "nanorod" means an elongated rod-like structure having a narrowest dimension diameter of less than 800 nanometers (nm).

[0039] In one embodiment of a method of making elongated nanostructures according to one embodiment of the invention, as shown in FIGS. 1A-1D, a plurality of catalyst particles 112 is deposited on an inorganic substrate 110. The substrate 110 could be made of one of several materials, for example: an oxide, a metal, or an elemental semiconductor. In some embodiments, inorganic monocrystalline substances would be preferable, while in other embodiments a polycrystalline material or an amorphous glass would be preferable. Some specific examples of suitable substrate materials include silicon, sapphire, and silicon carbide.

[0040] The catalyst particles 112 could include gold, nickel or cobalt and may be deposited in one of several ways. In one method of applying the catalyst particles 112 to the substrate 110, a thin film of the catalyst is applied to the substrate 110 and is heated to a temperature sufficient to cause the catalyst to enter a liquid phase, thereby causing the catalyst to agglomerate so as to form spatially-separated particles 112. The thin film would typically have a thickness of between 3 nm and 10 nm and could be applied to the substrate 110 by such methods as electron beam evaporation or sputtering. In another example of a way in which the catalyst particles 112 may be applied to the substrate 110, the catalyst particles 112 are deposited within a porous template (such as anodized aluminum oxide or silicon dioxide) to initiate growth. A

patterned film of the catalyst may be applied to the substrate 110 so as to control the shape and distribution of the catalyst particles 112.

[0041] In yet another example of a way in which the catalyst particles 112 may be applied to the substrate 110, a plurality of nano-particles 112 of the catalyst is suspended in an organic solvent, such as alcohol or acetone and a surfactant to inhibit agglomeration of the nano-particles 112. The nano-particles 112 and the solvent are applied to the substrate 110 and the nano-particles 112 are then dispersed with a spin coater.

[0042] The catalyst particles 112 and the substrate 110 are exposed to a metal-containing vapor 114, thereby forming elongated inorganic nanostructures 116 (such as nanorods, nanoribbons and nanobelts) between the substrate 110 and the catalyst particles 112. Examples of metals that may be used in the metal-containing vapor 114 include molybdenum, niobium, hafnium, silicon, tungsten, titanium, zirconium or tantalum.

[0043] The inorganic nanostructures 116 are then exposed to a carbon-containing vapor source 118, such as methane, ethylene, ethane, propane, or isopropylene. A reducing gas, such as hydrogen may also be added. This carburizes the inorganic nanostructures 116, thereby making a plurality of elongated carbide nanostructures 120. The nanostructures 120 may be either fully carburized or partially carburized. The elongated carbide nanostructures 120 and the catalyst particles 112 are then etched with an etchant 122 to remove the catalyst particles 112.

[0044] An electrically conductive buffer layer 211, as shown in FIGS. 2A-2D, may be applied to the substrate 110 prior to the step of applying a plurality of spatially-separated catalyst particles 112 to the substrate 110. The buffer layer 211 acts as a diffusion barrier and inhibits the formation of unwanted structures, such as silicides, due to interaction between the reactants and the substrate 110. The buffer layer 211 could include, for example, germanium carbide or silicon carbide applied in an epitaxial process, or a polycrystalline diffusion barrier such as W or Ti-W. In

some cases the buffer layer 211 should be suitable to support epitaxial growth of the nanostructure materials of interest. In other cases, epitaxy may not be necessary.

[0045] A field emission device 300, according to one embodiment of the invention, is shown in FIGS. 3A-3E. Such a device could be employed with one of many devices, including, for example, an imaging system and a lighting system. The field emission device 300 is made by applying a dielectric layer 314 to the substrate 310 and then a conductive layer 316 to the dielectric layer 314. The dielectric layer 314 typically includes a material such as silicon dioxide, silicon nitride, silicon oxynitride, or aluminum oxide. A cavity 317 is formed in the conductive layer 316 and the dielectric layer 314. Catalyst particles 312 are placed on the substrate 310 in the cavity 317 and nanorods 318 are grown and carburized within the cavity 317, according to the methods described above with reference to FIGS. 1A-1D. The nanorods 318 are typically made from a material such as a carbide, an oxide, a nitride, or an oxycarbide or a silicide. As disclosed above, a patterned catalyst film may be applied within the device cavity. The patterning could be done by photolithography, imprint lithography, e-beam lithography, chemical lithography, or any other method of patterning a thin film.

[0046] An electrical field, from a field source 322 may be applied to the catalyst particles 112 and the substrate 110 while they are exposed to the metal-containing vapor 114 to influence the direction of growth of the inorganic nano-structures 116.

[0047] In another embodiment, a conductive platform 420, as shown in FIG. 4, may be disposed on the substrate 310 within a cavity formed in the dielectric layer 314. At least one channel 402 is formed in the conductive platform 420 and a catalyst particle 404 is placed within the channel 402. Nanorods 418 are then grown so as to extend from the top surface of the conductive platform 420. The conductive platform 420 may be made of a material such as silicon or molybdenum. In one embodiment, the conductive platform 420 is a conic-shaped member having a relatively large bottom surface opposite the top surface. In one illustrative embodiment, the material of the conductive platform 420 is applied using an evaporation process while the substrate 310 is held at an angle and is rotated, thereby forming a conic shape. If a

voltage source (not shown) is applied to the substrate 310 and the conductive layer 316, then the nanorods 418 will emit electrons. Alternately, rather than forming a channel 402 in the conductive platform 420, the nanorods 418 may be grown from the top surface of the conductive platform 420. In one embodiment the material for the platform 420, as noted above, is aluminum oxide (alumina), but it could also be an insulating metal oxide that can be anodized to form nanopores.

[0048] In another embodiment, an aluminum metal support is deposited. The aluminum metal support is subsequently anodized to become a nano-porous aluminum oxide. Catalyst is placed within the pore bottoms and then nanorods are grown. The nano-porous anodized aluminum oxide (AAO) acts a template so that vertically aligned nanostructures are formed. The catalyst film may be put down first followed by the aluminum deposition. Alternately, there are several ways to ensure that catalyst is not plated on the surface within the cavity surrounding the AAO support. These include: (a) Reflow the photoresist so that it covers the Si surface adjacent to the aluminum support, then anodize; (b) Deposit a silicon nitride layer down prior to SiO_2 layer, then dry etch a hole into the nitride so Si is exposed, then deposit aluminum, then electroplate Au. It will not deposit on the silicon nitride because there is not electrical contact; (c) Place a sacrificial oxide layer on top of the nitride so that any material that deposits there during nanowire growth may be sacrificially removed by wet etching. In this case the trench would be etched by a dry etching method so it is directional and stops just above the nitride in the oxide layer.; (d) Use approach (b) but first deposit a gold film so that electroplating is not necessary.

[0049] A micrograph of a nanorod 510 made according to one embodiment of the invention is shown in FIG. 5A, a micrograph of a nanobelt 512 made according to one embodiment of the invention is shown in FIG. 5B, and a micrograph of a polycrystalline nanorod 514 made according to one embodiment of the invention is shown in FIG. 5C. The polycrystalline nanorod 514 could be made from a material such as, for example, molybdenum carbide, molybdenum silicide, or niobium carbide. As can be seen from the micrographs shown in FIGS. 5A-5C, nanostructures made

according to the methods described above typically have a smaller dimension of less than 800 nm.

[0050] One initial proof of concept experiment was carried out with a Mo_2C system. MoO_3 powder was placed in a tube furnace and a silicon wafer coated with a 10 nm Au film was placed downstream (about 1-5 cm) away on a (111)-oriented silicon wafer.

The system was heated to 900°C. Hydrogen and argon were applied at a flow rate of 300 standard cubic centimeters per minute (sccm) H_2/1000 sccm Ar for 5 min and CH_4 in a concentration of 300/1000 sccm for 10 minutes. Similar recipes at 850°C and 950 °C have also been attempted, and one run on sapphire with a similar catalyst has been tried. The results were that a mixture nanorods and nanoribbons were found on the substrate, which were determined by transmission electron microscopy (TEM) to be nanocrystalline in nature. In one such experiment, field emission with low turn on field (~1.25 V/um) and high current (up to 300 μA) was measured.

[0051] One embodiment of the invention includes a method for synthesis of carbide nanorods and related nanostructures by synthesis of metal oxide nanorods via the vapor-liquid-solid (VLS) mechanism, or a solid state nanowire growth mechanism, followed by in situ reduction and subsequent carburization. These nanostructures may find utility in gated field emission devices. In one embodiment, growth occurred below the eutectic temperature for VLS to take place (e.g., about 1053 C for the Mo-Au system) so growth took place in the solid state.

[0052] In one embodiment of the invention is to synthesize oxide nanorods and ribbons using the Vapor-Liquid-Solid (VLS) or related mechanisms for nanostructure growth (e.g., solid state growth mechanisms). In the VLS technique metal vapor that will be part of the composition of the carbide material is fed to appropriate nano-catalyst particles on the substrate surface such that the metal is dissolved and the catalysts become supersaturated. The metal then precipitates as a nanorod and presumably reacts with a CO or residual oxygen to form an oxide nanorod. The oxide nanorods are reduced and/or carburized in situ immediately after growth. If one can

control the position of catalyst islands by a secondary means, such as a block copolymer templates or electron beam lithography, then the lateral density of nanorods can be controlled. Alternatively, if a mixed phase is formed, then it may be possible to preferentially etch out one phase such that the density of rods is again diminished controllably. Low nanorod density is desirable to minimize electric field shielding when nanorods are too close together. This process can be carried out within a gated or ungated field emission or other device structure.

[0053] The choice of substrate is important. Potential substrates include, for example, silicon, sapphire, and silicon carbide. Silicon will react with the catalyst particles and the metal vapor to form a silicide which, in some cases, may be undesirable. This issue may be overcome by use of a suitable buffer layer. The desirable features of the buffer layer are that it should have the proper epitaxial relationship with the substrate and carbide nanorod (intermediate lattice mismatch with low strain), be a sufficient diffusion barrier for silicon or other elements, have an intermediate thermal expansion coefficient, and be electrically conducting. This last feature is important if a buffer layer is to be used on a semiconducting or insulating substrate. An example of such a buffer layer material is GeC or SiC. However, in some cases it may not be necessary to use an epitaxial buffer layer, in which case a simple diffusion barrier such as a tungsten thin film or Ti-W thin film may be sufficient. It may also be necessary to grow the rods at an appropriate temperature and then carburize at a higher (or lower) temperature. After processing, the metal nanocatalyst may be preferentially etched from the tip of the nanorods and ribbons using an appropriate etchant. It is also possible to grow the metal/oxide nanorods via an oxide-assisted growth mechanism, which does not require a catalyst, or an auto-catalytic process, and then carburize the nanorods. Other structures, such as nano-platelets may also be grown.

[0054] In another embodiment, nanorods could be included in a diode structure. Such a diode structure includes a substrate with the nanorods on it, with an anode on the opposite side of the substrate. An electric potential is directly applied between the substrate, which acts as a cathode and a spaced-apart anode plate, with no intermediate gate structure. The processing of this embodiment may be less

expensive than other methods and the resulting electric field may be sufficient for applications such as fluorescent lighting.

[0055] The above described embodiments are given as illustrative examples only. It will be readily appreciated that many deviations may be made from the specific embodiments disclosed in this specification without departing from the invention. Accordingly, the scope of the invention is to be determined by the claims below rather than being limited to the specifically described embodiments above.